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Hierarchical self-assembly of two-length-scale multiblock copolymers

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Abstract

The self-assembly in diblock copolymer-based supramolecules, obtained by hydrogen bonding short side chains to one of the blocks, as well as in two-length-scale linear terpolymers results in hierarchical structure formation. The orientation of the different domains, e.g. layers in the case of a lamellar-*in*-lamellar structure, is determined by the molecular architecture, graft-like versus linear, and the relative magnitude of the interactions involved. In both cases parallel and perpendicular arrangements have been observed. The comb-shaped supramolecules approach is ideally suited for the preparation of nanoporous structures. A bicontinuous morphology with the supramolecular comb block forming the channels was finally achieved by extending the original approach to suitable triblock copolymer-based supramolecules.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

During the 1990s conductive polymer blends based on polyaniline (PANI) were introduced. Interesting observations made included the observation of the liquid crystalline behavior of PANI protonated with camphor sulfonic acid (CSA) in m-cresol and the presence of a fractal interpenetrating network of fibrillar PANI(CSA) within a PMMA matrix in spin-cast blends of PANI(CSA) and PMMA from m-cresol [1, 2]. The first observation prompted Fredrickson to address theoretically the stiffening of flexible polymers by complexing with amphiphilic short chain surfactants [3]. Inspired by these observations we introduced poly(4-vinylpyridine) (P4VP) hydrogen bonded with pentadecyl phenol (PDP) as a model system to study in detail the properties of these so-called comb-shaped supramolecules [4]. As it turned out, the behavior of pure P4VP(PDP) systems was considerably more interesting than that of P4VP(PDP) solutions. SAXS studies of pure P4VP(PDP)$_{1.0}$ (the subscript denotes the number of PDP molecules per pyridine group) revealed this system to microphase separate into a short-length-scale lamellar structure with a long period of ∼3.5 nm at the order–disorder temperature (ODT) of ca. 65 °C (figure 1) [5]. In the next step the P4VP homopolymer was replaced by diblock copolymers of P4VP and polystyrene (PS) thus leading to PS-*b*-P4VP(PDP) supramolecules, with PDP hydrogen bonded to the P4VP block. The presence of two length scales, the large length scale of the diblock copolymer (i.e. its radius of gyration) and the short length scale of the 'repeat unit' of the comb-shaped P4VP(PDP) block, led to the formation of hierarchically ordered structures such as lamellar-*in*-lamellar, cylinders-*in*-lamellar, etc (see figure 2) [7]. In this paper we will address recent developments in the field of hierarchically ordered two-length-scale block copolymer(-based) systems.

2. Hierarchical structure formation and domain orientation

Both in the case of lamellar-*in*-lamellar, as shown by TEM (figure 2), and cylinder-*in*-lamellar, as shown by SAXS of the shear-aligned PS-*b*-P4VP(PDP) supramolecules (figure 3) [8], the short-length-scale structure is oriented perpendicular to the long-length-scale structure. Apparently, this is a consequence of the graft-like nature of the supramolecules. The molecular architecture of PS-*b*-P4VP(PDP) supramolecules resembles that of ternary C-*b*-(A-*graft*-B)$_n$ linear-graft diblock copolymers. For a graft copolymer with grafts that are regularly spaced, the graft together with the backbone in between the graft and its neighboring graft (i.e. A-*g*-B) can be considered as the repeat unit (figure 4). Whether such a graft copolymer will microphase separate obviously depends on the size and composition of this

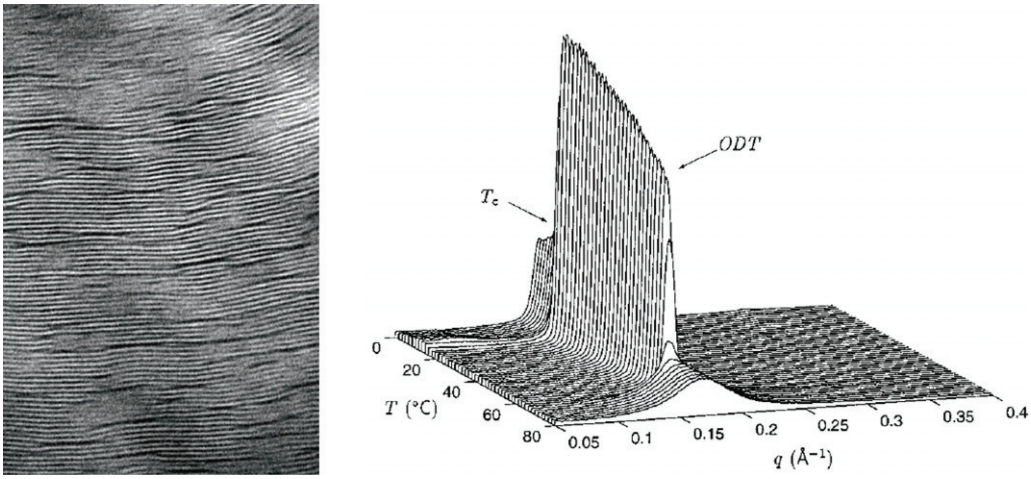

Figure 1. TEM (left) and SAXS (right) of P4VP(PDP)$_{1.0}$. ODT indicates the order–disorder transition temperature and T_c indicates the crystallization temperature of the pentadecyl tails [5, 6].

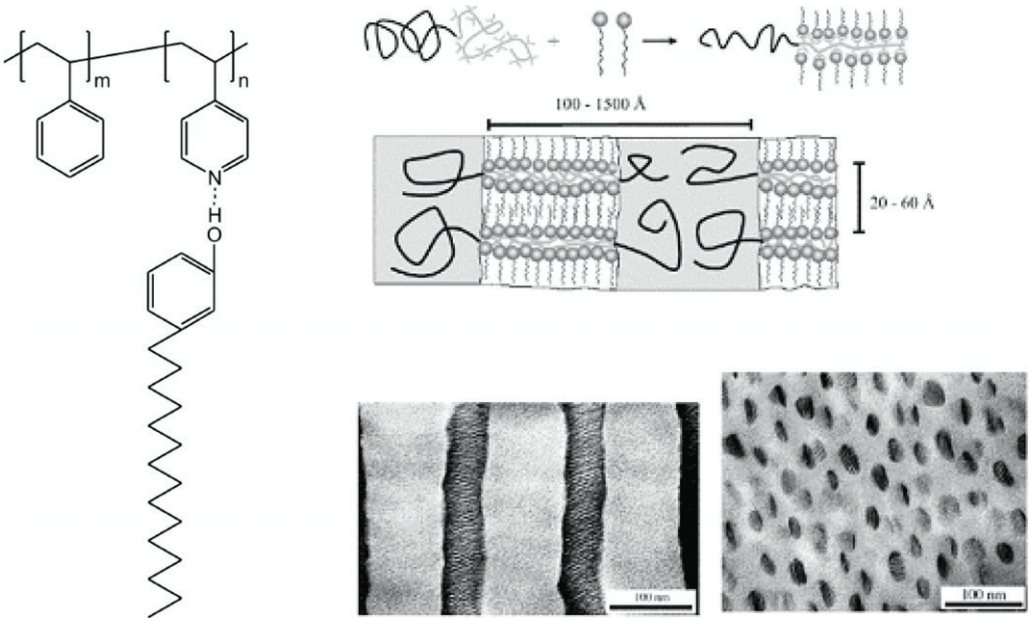

Figure 2. Illustration of a PS-*b*-P4VP(PDP)$_{1.0}$ supramolecule (left) and its lamellar-*in*-lamellar and lamellar-*in*-sphere self-assembly [7].

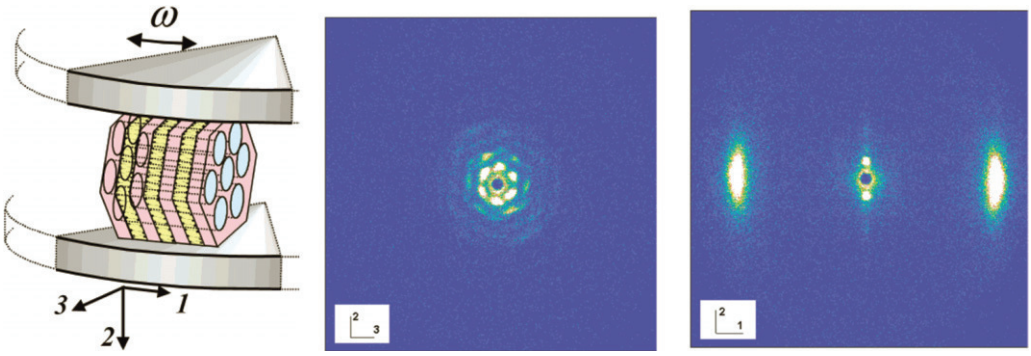

Figure 3. Cartoon of the shear-aligned cylinder-*in*-lamellar morphology of PS-*b*-P4VP(PDP). Tangential SAXS (middle) and radial SAXS confirm the relative orientation of layers and cylinders as shown in the cartoon [8].

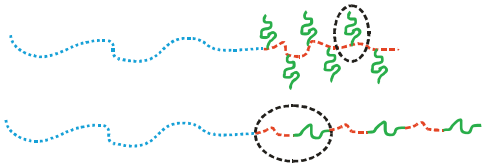

Figure 4. Schematic illustration of two-length-scale molecular architectures.

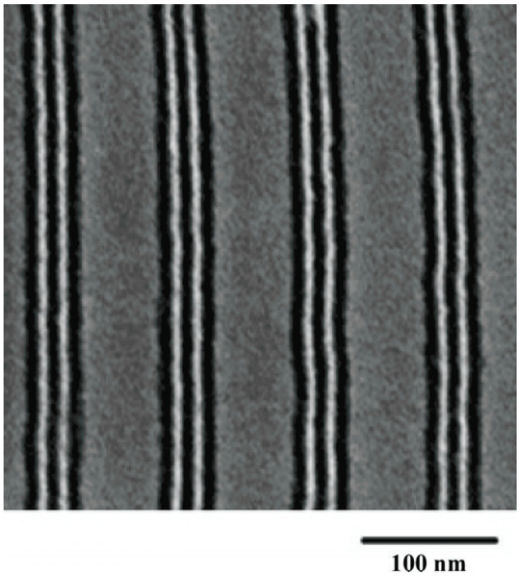

Figure 5. Parallel lamellar-*in*-lamellar morphology of P2VP-*b*-[(PI-*b*-PS)$_4$-*b*-PI]-*b*-P2VP undecablock copolymers [9] (courtesy of Professor Yushu Matsushita).

repeat unit. The characteristic property of our diblock copolymer-based supramolecules is the presence of two different length scales due to the relatively short length scale associated with the repeat unit of the P4VP(PDP) block. Although the linear-graft diblock copolymer closely resembles our supramolecules, the consequences of the two different length scales can be studied just as well for the corresponding linear molecular architecture (figure 4), where it will also result in hierarchical structure formation. Indeed, very recently the self-assembly of C-*b*-[(A-*b*-B)$_n$-*b*-A] and C-*b*-[(A-*b*-B)$_n$-*b*-A]-*b*-C multiblock terpolymer systems has become an active area of research [9–15], and for lamellar-*in*-lamellar morphologies both the perpendicular and parallel arrangements have been observed. The conditions leading to the stability of either of these have been discussed theoretically as well. For systems of interest, the layers of the relatively large C-block are separated by layers of the $(A\text{-}b\text{-}B)_n\text{-}b\text{-}A$ multiblock copolymer, which in turn contains internal layers of A- and B-blocks. Theoretical considerations confirm that the orientation of these 'thin' layers with respect to the 'thick' layers is either parallel or perpendicular depending mainly on the relative magnitude of the unfavorable B–C interactions as expressed in the corresponding χ_{BC} Flory–Huggins parameter [13, 15]. Matsushita and co-workers [9] were the first to investigate the hierarchical self-assembly of two-length-scale ternary multiblock copolymers consisting of poly(2-vinylpyridine) (P2VP), polyisoprene (PI) and polystyrene

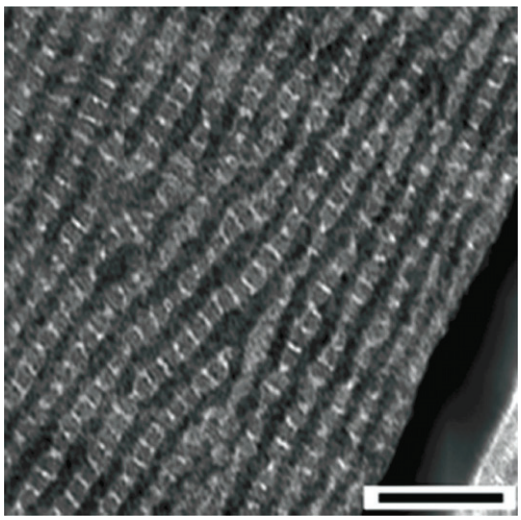

Figure 6. Perpendicular lamellar-*in*-lamellar morphology for a C-*b*-[(A-*b*-B)$_2$-*b*-A] multiblock copolymer, A = poly(cyclohexylethylene), B = polyethylene and C = poly(ethylene-alt-propylene). The scale bar indicates 100 nm. Reprinted with permission from [10]. © American Chemical Society Copyright 2009.

(PS). For the P2VP-*b*-[(PI-*b*-PS)$_4$-*b*-PI]-*b*-P2VP undecablock copolymer with a molar mass of 339 000 g mol^{-1} and composition (volume fractions) P2VP:PI:PS = 0.53:0.26:0.21 a lamellar-*in*-lamellar morphology with 5 'thin' internal layers was observed. As figure 5 illustrates, in this case the different layers are parallel. The interaction parameter values for the pairs PS/PI and PS/P2VP are both of the order of 0.1. The interaction between PI and P2VP is not well known, however, estimates suggest it to be considerably larger than the other two. If the interaction between the not directly connected blocks, i.e. the outer C- and the inner B-blocks of C-*b*-[(A-*b*-B)$_n$-b-A] or C-*b*-[(A-*b*-B)$_n$-*b*-A]-*b*-C multiblock terpolymers, is considerably less unfavorable than that between the directly connected C- and A-blocks, the arrangement where the inner layers are oriented perpendicularly with respect to the confining layers, thus also creating a C/B interface at the expense of the C/A interface, becomes an alternative possibility. It was first observed by Fleury and Bates [10] for the C-*b*-[(A-*b*-B)$_2$-*b*-A] multiblock terpolymer with A, B and C representing poly(cyclohexylethylene), polyethylene and poly(ethylene-alt-propylene), respectively (figure 6). Here the interaction parameter values are $\chi_{AB} \cong 0.054$, $\chi_{AC} \cong 0.034$ and $\chi_{BC} \cong 0.0054$. Apparently χ_{BC} is sufficiently smaller than χ_{AC} ($\chi_{BC}/\chi_{AC} \cong 0.16$) to force the formation of B–C interfaces.

Very recent self-consistent field and strong segregation analytic calculations have confirmed the thermodynamic stability of the perpendicular orientation of C-*b*-[(A-*b*-B)$_n$-*b*-A] multiblock copolymers for χ_{BC}/χ_{AC} sufficiently small [11, 15]. In [13] it was shown on the basis of a strong segregation analysis that the perpendicular orientation should become the stable morphology for $\chi_{BC}/\chi_{AC} < 0.22$ in the case of equal volume fractions of C and $(A\text{-}b\text{-}B)_n\text{-}b\text{-}A$, provided n is sufficiently large. A characteristic phase diagram is presented in figure 7 for $n = 10$.

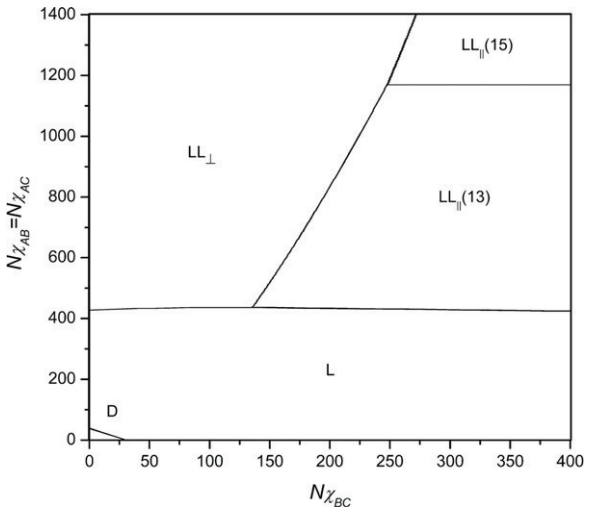

Figure 7. Phase diagram of C-*b*-(A-*b*-B)$_n$-b-A for $n = 10$ with $\chi_{AB} = \chi_{AC}$. In the parallel lamellar-*in*-lamellar structure $LL_{\parallel}(\cdot)$ the number in between the brackets denotes the number of thin layers [13].

Returning to the PS-*b*-P4VP(PDP)$_{1.0}$ self-assembled supramolecules, we showed that both the lamellar-*in*-lamellar and cylinder-*in*-lamellar are characterized by a perpendicular orientation of the two different structures. Much to our surprise, however, we observed this was not necessarily true in the case of PS-*b*-P4VP(PDP)$_{1.0}$ films. Thin films of PS-*b*-P4VP(PDP)$_{1.0}$ supramolecules, that self-assemble in the bulk in the form of PS cylinders inside a P4VP(PDP) matrix, were prepared by spin coating a chloroform solution on a SiO_2 substrate. During the annealing of these thin spin-coated films in chloroform vapor, the PS microphase separated from the disordered P4VP(PDP) phase and terraces of parallel oriented PS cylinders in a matrix of P4VP(PDP) were formed. Upon evaporation of the chloroform, the P4VP(PDP) combs dropped below their order–disorder transition temperature forming alternating layers of P4VP and PDP [16]. Due to the preferential interaction of P4VP with SiO_2 and of PDP with the air interface these layers were also oriented parallel to the substrate and hierarchical terrace formation occurred with terraces of the short P4VP(PDP) length scale inside terraces of the PS/P4VP(PDP) long length scale (figure 8).

3. Bicontinuous morphology

Block copolymer self-assembly plays an important role in recent developments in nanotechnology [17]. Ordered nanoporous structures may be prepared if one of the components can be selectively removed and may subsequently be used as, e.g., a nanoporous membrane [18] or for template purposes [19]. It is particularly in this area where the comb-shaped hydrogen-bonded supramolecules approach has a distinct advantage. The hydrogen-bonded side chains may simply be removed by dissolution, e.g., with ethanol in the case of PS-*b*-P4VP(PDP), thus rendering ordered

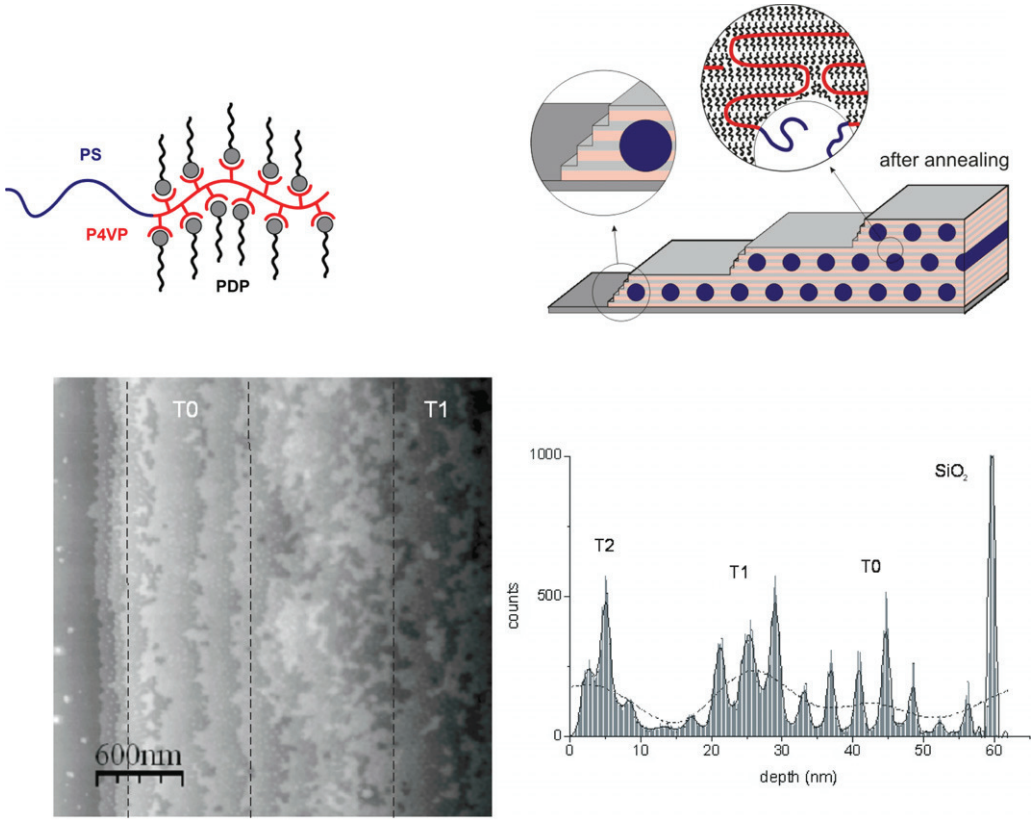

Figure 8. AFM height image and depth profile of PS-*b*-P4VP(PDP)$_{1.0}$ thin films on SiO_2. The black line is an FFT smoothing of the data, the distance between the small peaks is ∼4 nm. The dotted line is the result of more drastic data smoothing, from which it can be concluded that the smaller terraces are a part of three long-length-scale structures [16].

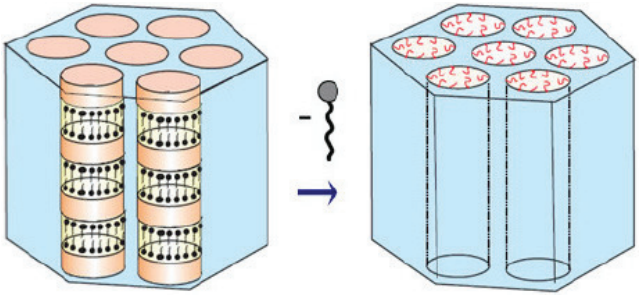

Figure 9. Illustration of the straightforward preparation of nanoporous channels by dissolving PDP away from the lamellar-*in*-cylinder self-assembled PS-*b*-P4VP(PDP) supramolecules.

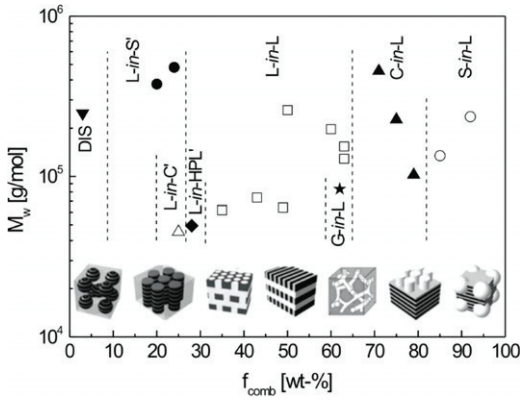

Figure 10. Morphology diagram of PS-*b*-P4VP(PDP)$_{1.0}$ as a function of the weight fraction of P4VP(PDP)$_{1.0}$ at room temperature. M_w refers to the total molecular weight of the complete supramolecule [30, 31].

nanoporous structures in a straightforward manner [20–22]. Figure 9 illustrates this procedure for the lamellar-in-cylinder morphology.

Many possible future applications require thin films. In that case the orientation of the cylinders is essential and the perpendicular orientation is for many applications the preferred state. But, as one of the components has in general the lowest interfacial/surface tension, a parallel rather than perpendicular orientation is the thermodynamic equilibrium state and special care has to be taken to arrive at the perpendicular one [23]. If continuous pathways from top to bottom through the film are required, the orientation problem can be avoided if a bicontinuous morphology is present. Several applications along this line have already been presented [24–26]. For our PS-*b*-P4VP diblock copolymer-based supramolecules this approach would correspond to a bicontinuous morphology with the P4VP(PDP) component forming the continuous network(s) inside a PS matrix. As is well known, for diblock copolymers the bicontinuous gyroid morphology is only found in the intermediate segregation regime of the phase diagram in between the cylindrical and lamellar structures [27]. Except for very small molar masses our PS-*b*-P4VP diblock copolymers are, however, in the strong segregation limit due to the large value of the interaction parameter ($\chi_{S,4VP} \cong 0.35$) [28]. Fortunately, the presence of PDP reduces the effective interaction between the PS phase and the disordered (i.e. above 65 °C) P4VP(PDP) phase and at elevated temperatures the PS-*b*-P4VP(PDP) system will generally be in the intermediate rather than strong segregation regime [29]. This implies that the gyroid morphology should become a distinct possibility. Practice shows this statement to be only partly true. Indeed, the bicontinuous morphology has been found but only in the case of PS being the minority phase and forming the bicontinuous networks (figure 10) [30]. Despite considerable efforts the gyroid morphology with P4VP(PDP) being the minority component forming the bicontinuous networks has never been observed for diblock copolymer-based PS-*b*-P4VP(PDP) systems. Although this excludes the preparation of membranes with bicontinuous network nanochannels it does not preclude the preparation of bicontinuous network samples for template purposes. The dissolution of PDP from the gyroid-*in*-lamellar structure with the majority component P4VP(PDP) forming the matrix will result in an open network structure with struts consisting of a PS core and a P4VP corona.

Systems where the nano-network channels are formed by P4VP(PDP) were ultimately achieved when we moved on to triblock copolymer-based hydrogen-bonded supramolecules [32, 33]. A specific triblock copolymer of poly(t-butoxystyrene) (PtBOS), polystyrene and poly(4-vinylpyridine) ($M_n = 76.0$ kg mol^{-1}, $f_{tBOS} = f_S = 0.41$, $f_{4VP} = 0.18$) with PDP hydrogen bonded to P4VP, i.e. PtBOS-*b*-PS-*b*-P4VP(PDP)$_x$, self-assembled into a bicontinuous morphology with P4VP(PDP) forming the network channels for the ratio x between the number of PDP molecules and the number of 4VP groups satisfying $0.3 \leqslant x < 0.8$ (figure 11) [33].

4. Outlook

Hierarchical structure formation has become an active area of research. In the examples discussed in this paper three different chemical species were always involved. Microphase separation in such systems will obviously result in ordered structures containing three chemically different domains. Here we briefly discussed the arrangement of these domains, e.g. parallel versus perpendicular, and showed how this is related to the molecular architecture and the interactions involved. The presence of three chemically different species, however, is not necessary to obtain hierarchically ordered structures. Indeed, a molecular architecture characterized by two length scales, such as a linear A-*b*-(B-*b*-A)$_n$-B multiblock copolymer with long A- and B-outer blocks and a (*A*-*b*-B)$_n$ multiblock consisting of short A- and B-blocks, already suffices. As shown theoretically, such systems may show very intriguing self-assembly behavior [34–38]. Experimental studies are still very scarce. Matsushita and co-workers [39] were the first to report a lamellar-*in*-lamellar morphology for a two-length-scale S–[I–S–I–S–I–S–I–S–I]–S undecablock copolymer of polystyrene (S) and polyisoprene (I). In between thick PS layers they observed three thin layers of PI, PS and PI. Very recently we observed a similar lamellar-*in*-lamellar morphology for a S–[HS–S–HS–S–HS–S]–HS octablock copolymer of polystyrene and poly(*p*-hydroxy styrene) (HS). Here the long end blocks are chemically different and the structure consists of thick PS and PHS layers. In between these thick layers a thin PHS

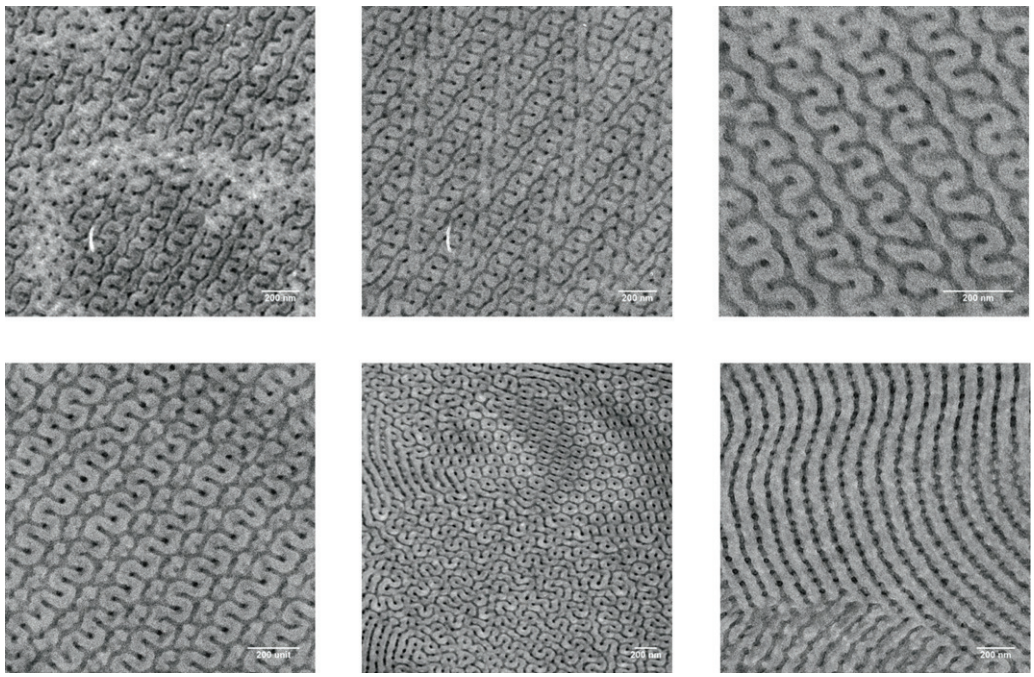

Figure 11. TEM of PtBOS-*b*-PS-*b*-P4VP(PDP)$_x$ ($M_n = 76.0$ kg mol^{-1}, $f_{tBOS} = f_S = 0.41$, $f_{4VP} = 0.18$). Top row (from left to right): $x = 0.3, 0.4, 0.5$. Bottom row (from left to right): $x = 0.6, 0.7, 0.8$.

followed by a thin PS layer was observed [40]. This is only the beginning and many more experiments will be required to resolve all the intricacies of these two-length-scale binary multiblock copolymer systems.

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